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A STUDY OF THE SYNTHESIS OF SOME DERIVATIVES OF BORAZENE BY GRIGNARD-TYPE REACTIONS

By

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INTRODUCTION

Borazene, a six-membered ring of alternate boron and nitrogen atoms, each bonded externally to a hydrogen, was discovered in 1926 by Stock and Pohland (28). They correctly assigned the ring structure to it on the basis of its chemical properties. This has been verified by electron diffraction studies which show that the compound is planar with bond angles of 120° (1, 4).

Because of the difficulty of its synthesis only slow progress has been made, until recently, in the study of its chemical behavior and in the preparation of different types of compounds containing the borazene ring. Originally the synthesis involved the pyrolysis of the addition product of ammonia and diborane (28), so that the synthesis of large quantities of borazene was not practical. Synthesis of N-alkyl substituted borazenes could be effected by starting with amines rather than ammonia (26). B-alkyl-borazenes have been synthesized by using boron trialkyls (25), alkyl boron dichloride (21), or by treating borazene with boron trimethyl (26). The synthesis of borazene has been facilitated by the use of lithium borohydride in place of diborane (23). Sodium borohydride has also been found to be practical for the synthesis (8). Jones and Kinney (11) found that N-aryl-B-haloborazenes could be synthesized from the reaction of boron trihalides and aromatic amines in an

aromatic solvent. This synthesis has been extended to include the reaction of ammonium chloride (3, 24) and alkyl amine hydrochlorides with boron trihalides. An alternate synthesis for borazene uses the reduction of B-trichloroborazene with lithium borohydride (24), or sodium borohydride (8).

Because boron may act as an electron pair acceptor and nitrogen may act as an electron pair donor, there is the possibility of internal pi bonds being formed, in addition to the usual sigma bonds. In accordance with this, some bond shortening is indicated in the ring (20), and borazene shows absorption in the ultraviolet region of the spectrum corresponding to mobile electrons (9, 18, 20). Because of this, some authors have assigned a double bond resonance structure to borazene (16). The internal coordination would have the result of placing a partial negative charge on the boron and a partial positive charge on the nitrogen. Because of this, the hydrogen on the boron is somewhat hydridic and the hydrogen on the nitrogen is somewhat acidic.

It is found that borazenes add hydrogen chloride, hydrogen bromide, water, methanol, ammonia, and diethyl ether. Some of these addition products decompose to give substituted borazenes. For example, the addition of hydrogen bromide to borazene ultimately results in the formation of B-tribromoborazene:

$$B_3H_3N_3H_3 + 3HBr \longrightarrow B_3H_3Br_3N_3H_6 \longrightarrow B_3Br_3N_3H_3 + 3H_2$$

Some cases of substitution reactions have been observed. Borazene will react with boron trimethyl to give B-trimethylborazene (26), and with boron trichloride and boron tribromide to give B-mono-, di-, or trichloroborazene and B-mono-, di-, or tribromoborazene, respectively (23).

It can be seen that the types of borazenes which have been prepared are few. In preparing derivatives of borazene it has been common to custom-build the borazene by use of the appropriate starting materials, rather than by working with the borazene group itself. The object of this research was to attempt to expand the field of borazene chemistry by finding general synthetic methods applicable to the preparation of borazene derivatives in good yields, and of different functional types. In the field of organic chemistry the use of organo-metallic compounds has been of tremendous value in the preparation of organic compounds of different classes. In particular the Grignard reagent, prepared from an organic halide and magnesium, has been invaluable. Since B-haloborazenes are easily prepared in quantity from readily obtainable starting materials, it was decided to attempt to prepare borazene analogs of Grignard reagents and to use these in the general preparations of other substituted borazenes.

EXPERIMENTAL PROCEDURES

Preparation of the B-trihaloborazenes

Since none of the B-trihaloborazenes used were commercially available, it was necessary to prepare them. The B-trihaloborazenes may be prepared by the halogenation of the appropriate borazene or by an adaptation of the method of Jones and Kinney (11), and Laubengayer and Brown (3), which involves the reaction of a boron trihalide with ammonium halide, or the appropriate amine hydrohalide, in an inert organic solvent. Since the latter method uses readily available chemicals and gives good yields of the B-trihaloborazenes, it was the method chosen. The reaction may be written in several steps as:

$$BX_3 + (RNH_3)X \longrightarrow BX_3{:}NH_2R + HX$$

$$BX_3{:}NH_2R \longrightarrow (BX_2NHR)_n + HX$$

$$(BX_2NHR)_n \longrightarrow B_3X_3N_3R_3 + HX$$

where R is either an organic radical or hydrogen.

Preparation of N-trimethyl-B-trichloroborazene

One neck of a two-liter, three-necked flask was fitted with a water condenser topped with a dry-ice condenser, which was connected to a dry-ice trap to catch any boron trichloride escaping the dry-ice condenser. The dry-ice trap was in series with a mineral oil bubbler to indicate hydrogen chloride evolution. The gas was passed to the

outside through the hood. The other side neck was fitted with a dry-ice condenser connected to a trap containing a weighed quantity of boron trichloride. The center neck was fitted with a stirrer if large quantities of reactants were used. A quantity of boron trichloride, not exceeding 600 grams, was condensed into a previously weighed trap, and the weight of boron trichloride taken. From this weight, the equivalent quantity of methylamine hydrochloride, based upon the above equations, was calculated and 95 per cent of this quantity was added to the flask along with 800-900 ml. of chlorobenzene. The mixture was heated to reflux with a Glas-col heating mantle and then the boron trichloride was added slowly at such a rate that the boron trichloride fell dropwise from the exit dry-ice condenser. Allowing the trap containing boron trichloride to stand at room temperature usually gave a satisfactory rate of boron trichloride addition. Otherwise the trap was warmed or cooled as necessary. Addition of the boron trichloride took from four to eight hours, depending upon the quantities used. If any boron trichloride escaped into the dry-ice trap, it was re-added. Excess boron trichloride was kept in the reaction system for six hours after its addition was completed, by keeping the exit dry-ice condenser filled. After this time the excess boron trichloride was allowed to escape into the dry-ice trap. As shown by the equations, hydrogen chloride is

produced during the reaction, and the rate of reaction may be followed by the rate of evolution of hydrogen chloride at the exit mineral oil bubbler. Reaction was continued at the reflux temperature of chlorobenzene until the evolution of hydrogen chloride ceased almost entirely. This required from thirty-six to forty-eight hours. After this time had elapsed, the mixture was transferred to another flask and the solvent removed. It was found most convenient to remove about three-fourths of the solvent by distillation at atmospheric pressure and the remainder by gentle warming with an oil bath with the flask at about 1 mm. Hg. Final removal of the solvent was effected by heating the flask in an oil bath at 80° C. for one to two hours, at 1 mm. Hg. Temperatures above this caused an excessive loss of product due to sublimation. After the removal of the solvent was completed, the flask and its contents were transferred to a vacuum sublimation apparatus and the product was sublimed. At about 1 mm. Hg, a bath temperature of 110-120° C. was required to give a reasonable rate of sublimation. The product consisted of white needles melting at 152-154° C. The yields, based upon the quantity of methylamine hydrochloride used, were quantitative. The product was stable, when stored in a dry box, for several months.

Analysis showed:	%B	%N	%Cl
Found	14.36	18.51	46.5
Calculated for $B_3Cl_3N_3(CH_3)_3$	14.36	18.59	47.1

When reaction times of six to ten hours were used two products were found. The first product was soluble in the solvent at room temperature and was identified as N-trimethyl-B-trichloroborazene from analysis, sublimation, and melting points. The second product was insoluble in the solvent at room temperature and crystallized as long white needles. It did not sublime at 1 mm. Hg until a bath temperature of 180° had been reached.

Analysis showed:	%B	%N	%Cl
Found	9.26	11.22	64.21
Calculated for $(CH_3NHBCl_2)_n$	9.68	12.53	63.44
Calculated for $CH_3NH_2{:}BCl_3$	7.30	9.45	71.75

From the analysis it seems probable that this product was either CH_3NHBCl_2 or its polymer. On the basis of its low volatility it could be the trimer or a relatively low molecular weight polymer. Without molecular weight data no distinction between these possibilities could be made. Addition of fresh solvent to this solid and continued refluxing resulted in additional hydrogen chloride evolution and formation of more N-trimethyl-B-trichloroborazene.

Besides chlorobenzene, xylene was used as a solvent

in some of the preparations. Chlorobenzene is apparently more inert than xylene and gives better yields and a cleaner-appearing system at the completion of the reaction. A pure white product is more readily obtained when chlorobenzene is used. The commercial chlorobenzene, which was used without further purification, showed a wide variation from lot to lot in the quantity of dark, tarry material produced.

Matheson technical grade boron trichloride was used as condensed from a lecture bottle. A small amount of non-volatile material usually remained in the trap after addition of boron trichloride was completed.

The methylamine hydrochloride used was obtained from Eastman, Fisher and Matheson, and Coleman and Bell. It was dried over calcium sulfate in a desiccator before use.

Preparation of B-trichloroborazene

The apparatus was similar to that described above, but in this case stirring is essential. Ground glass, used by other authors as a dispersant for the ammonium chloride (23), was omitted with only a slight loss of yield. The same general procedure as outlined above for the preparation of N-trimethyl-B-trichloroborazene was followed, but with smaller quantities of reactants. The maximum quantities of reactants used were 292 grams (2.49 moles) of boron trichloride, 128 grams (2.4 moles) of ammonium chloride,

and 700 ml. of chlorobenzene. Complete addition of boron trichloride required slightly more time than during the previous preparation. However, the reaction was usually finished, as judged from the cessation of hydrogen chloride evolution, within an hour after the addition of boron trichloride was completed.

After the reaction was completed the contents of the flask were transferred to another flask, and about half of the solvent was removed by distillation at atmospheric pressure. The remainder of the solvent was removed under reduced pressure (.5 mm. Hg) with the flask at room temperature. It was necessary to keep the flask cool, in contrast to the previous preparation, because of the greater volatility of B-trichloroborazene as compared with N-trimethyl-B-trichloroborazene. After the solvent had been removed the B-trichloroborazene was sublimed as white crystals. The yield varied from 55 to 60 per cent.

Analysis showed:	%B	%N-H	%Cl
Found	17.63	24.42	58.15
Calculated for $B_3Cl_3N_3H_3$	17.65	24.51	57.86

If more than a month had elapsed since purification, it was necessary to resublime the material before use.

No attempt was made to improve the yield reported above. The lower yield of B-trichloroborazene, as compared to N-trimethyl-B-trichloroborazene, could be attributed to

the thermal instability of the former. This compound is known to be unstable (8) at the temperatures used during its preparation. Thus, during the course of the reaction, a time will be reached at which B-trichloroborazene is decomposing more rapidly than it is being produced by the reaction. Therefore the yields could not be improved by increasing the reaction time as was done in the preparation of N-trimethyl-B-trichloroborazene.

A solid residue, probably a boron nitride, is always found in the reaction flask. This solid residue was separated from the liquid only by decantation, so some of the solid was transferred to the sublimation flask, but this caused no apparent harm. Other authors (24) have centrifuged the mixture to remove the solid.

Preparation of N-trimethyl-B-chloro-B-bromoborazenes

Since boron tribromide is less volatile than boron trichloride, techniques somewhat different from those necessary for handling the previous preparations were used. The center neck of a two-necked flask was fitted with a reflux condenser connected to a mineral oil bubbler to indicate hydrogen halide evolution. After addition of chlorobenzene and methylamine hydrochloride to the reaction flask, a 5 per cent excess of boron tribromide was quickly measured with a pipet and added to the flask contents. The mixture was refluxed for forty hours. Throughout this time

hydrogen halide was slowly evolved. Insoluble material was formed during the first hour of reaction and remained throughout the reaction period. After the reaction mixture was cooled, the supernatant liquid was decanted from the solid. The solvent was removed under reduced pressure and the N-trimethyl-B-chloro-B-bromoborazene sublimed at an oil bath temperature of 120 to 135° C. and 1 mm. Hg. The yield, which is based upon the average molecular weight of 301, calculated from the analysis given below, was 42 per cent. No additional product was recovered by adding fresh solvent to the flask residue and further refluxing.

Analysis showed:	%B	%N-CH_3	%Cl	%Br
Found	10.85	29.16	16.04	43.94
Calculated for $B_3Cl_3N_3(CH_3)_3$	14.36	38.54	47.10	0.00
Calculated for $B_3Br_3N_3(CH_3)_3$	9.03	24.23	0.00	66.72

The product prepared from this reaction is apparently a mixture of N-trimethyl-B-trichloroborazene, N-trimethyl-B-dichloro-B-bromoborazene, N-trimethyl-B-chloro-B-dibromoborazene, and N-trimethyl-B-tribromoborazene. This preparation will be discussed more fully in another section of this dissertation.

Preparation of B-tribromoborazene

The apparatus and procedure were similar to those

given above for N-trimethyl-B-chloro-B-bromoborazene. However, the average time of reaction was twelve hours. Stirring seemed to have the unexpected result of decreasing the rate of hydrogen bromide evolution, and consequently was not used. In a typical reaction 155 grams (1.58 moles) of ammonium bromide, 404 grams (1.67 moles) of boron tribromide, and 800 ml. of chlorobenzene were used. The average yield was about 100 grams (.315 moles) of purified product. The average yield was 60 per cent, but was as high as 80 per cent when smaller quantities of starting material were used.

Melting point, found	125-127° C.
Melting point, literature (24)	126-128° C.

Analysis showed:	%B	%N	%Br
Found	10.18	12.97	74.56
Calculated for $B_3Br_3N_3H_3$	10.23	13.25	75.57

If storage time exceeded one month, the B-tribromoborazene was resublimed before use.

Reaction of B-trihaloborazenes with Magnesium

Reaction of N-trimethyl-B-trichloroborazene with magnesium

Ethyl ether, 15 grams (.066 moles) of N-trimethyl-B-trichloroborazene, 5 grams (.206 moles) of magnesium, and a small crystal of iodine were added to a round-bottomed

flask fitted with a reflux condenser vented to the atmosphere through a drierite column. No spontaneous reaction occurred with gentle warming. The mixture was refluxed for several hours with no apparent effect. After refluxing was stopped, the solvent was distilled at reduced pressure and the unreacted N-trimethyl-B-trichloroborazene recovered by sublimation at reduced pressure. In addition to the N-trimethyl-B-trichloroborazene a small amount of gummy material was found.

Tetrahydrofuran is a more powerful solvent for Grignard reactions than ethyl ether. Consequently, tetrahydrofuran, dried with sodium and calcium hydride, was tried as a solvent. The same quantities of reactants as described above were used. The iodine color completely disappeared in about ten minutes, but no spontaneous reaction started. The mixture was refluxed for several hours. During this time the magnesium darkened and etched considerably and the solution turned a reddish color. The solution was decanted from unreacted magnesium and the solvent distilled under reduced pressure. No N-trimethyl-B-trichloroborazene could be recovered from the mixture at the normal sublimation temperature. A light brown solid remained.

Analysis of the solid showed:

%B	%N	%Mg	%Cl
10.3	13.7	6.03	28.3

This analysis gives an empirical formula corresponding to $B_3N_3Cl_{2.46}Mg_{.75}(C_4H_8O)$, if the remainder is assumed to consist of only tetrahydrofuran. This result can be explained by assuming a mixture such as $B_3N_3(CH_3)_3Cl_2MgCl$ and $B_3N_3(CH_3)_3Cl_2\text{-}Mg\text{-}B_3N_3(CH_3)_3Cl_2$.

Reaction of N-trimethyl-B-chloro-B-bromoborazene with magnesium

An attempt was made to react N-trimethyl-B-chloro-B-bromoborazene with magnesium in refluxing ethyl ether with iodine as a catalyst. No reaction was observed.

Reaction of B-trichloroborazene with magnesium

This compound also failed to react with magnesium in refluxing ethyl ether with iodine as a catalyst.

Reaction of B-tribromoborazene with magnesium

In contrast to the above compounds, B-tribromoborazene showed a very vigorous, spontaneous reaction with magnesium in the presence of ethyl ether, even without a catalyst. It was found that 1.5 moles of magnesium were consumed for each mole of B-tribromoborazene present in the reaction mixture. Two liquid layers were formed as the spontaneous reaction neared completion. The top layer was colorless, clear, and ether soluble. The bottom layer was gray, cloudy, viscous, and immiscible with ethyl ether. Neither layer showed further reaction with magnesium. Also,

neither layer reacted with methyl iodide. Neither layer showed any tendency to couple with N-trimethyl-B-trichloroborazene. When magnesium was added slowly to a solution of B-tribromoborazene in ethyl ether a precipitate was formed. As more magnesium was added, the precipitate went into solution, or suspension, giving a two-layer mixture similar to that observed above at the completion of the reaction.

No reaction was observed between B-tribromoborazene and magnesium in refluxing benzene, even with iodine added as a catalyst.

Removal of the solvent from the above layers at room temperature and 1 mm. Hg gave white solids.

Analysis showed:	%B	%N	%Br	%Mg	% Remainder
Top-layer residue	9.85	13.89	28.9	7.83	39.53
Bottom-layer residue	3.41	4.52	50.47	8.31	33.29

If the remainder is arbitrarily assigned to ethyl ether, which may be present as a complex, an etherate, or may be trapped in the solid, we get atom ratios of

$B_3N_3MgBr(Et_2O)_{1.5}$ for the solid from the top layer, and

$B_3N_3Mg_3Br_6(Et_2O)_{4.5}$ for the solid from the bottom layer.

Upon pyrolysis at 100 to 250° C. and 1 mm. Hg, the solids from both layers gave small amounts of a colorless liquid. The liquids from both layers had identical infrared spectra and gave the same analysis for boron and nitrogen, so it was concluded that both layers gave the same pyrolysis

product. The liquid distilled at 65 to 66° C. (.4 mm. Hg).

Analysis showed:	%B	%N
Top-layer pyrolysis product	16.14	20.40
Bottom-layer pyrolysis product	16.27	20.30

Analysis of the combined liquids showed:

	%B	%N	%C	%H	%O
Found	16.29	20.14	37.36	8.80	17.41
Calculated for:					
$B_3(OC_2H_5)_3N_3H_3$	15.26	19.76	33.88	8.53	22.57
$B_3C_2H_5(OC_2H_5)_2N_3H_3$	16.50	21.37	36.64	9.22	16.27
$B_3(C_2H_5)_2OC_2H_5N_3H_3$	17.96	23.26	39.88	10.04	8.86

(the oxygen content was found by difference)

This data, considering that the nitrogen usually comes out about 5 per cent low, seem to indicate that the product was predominantly B-ethyl-B-diethoxyborazene.

The top layer from the reaction between B-tribromo-borazene and magnesium in ethyl ether reacted exothermically with n-butyl magnesium bromide to give a two-layer system. No liquid products were isolated from the bottom layer, which was probably the etherate of magnesium bromide. The top layer gave a liquid with a boiling point range from 40 to 160°C. (.4 mm. Hg).

	%B	%N
Analysis of 40-80° C. fraction showed	10.44	10.57
Analysis of 80-160°C. fraction showed	12.47	14.75

The last part of the high boiling fraction was less volatile than would be expected for a product monomeric in borazene rings, so it is possible that the liquid contained coupled borazene rings.

A reaction between magnesium and B-tribromoborazene was carried out in the presence of N-trimethyl-B-trichloroborazene. A solution of 30.1 grams (.133 moles) of N-trimethyl-B-trichloroborazene in 150 ml. of ethyl ether, and 2.3 grams (.09 moles) of magnesium was placed in a 300 ml. two-necked flask. Then a solution of 10 grams (.032 moles) of B-tribromoborazene in ethyl ether was added slowly. The reaction was slow and lasted for about an hour, after which the mixture was refluxed gently. A white precipitate formed slowly during the course of the reaction. Only one layer was present in this reaction, indicating that only relatively small amounts of magnesium bromide were formed. The white precipitate was filtered through a fritted disc Buchner funnel, washed with ethyl ether, and then kept at about 1 mm. Hg at room temperature overnight to remove excess ethyl ether. The precipitate was soluble in hot water. The precipitate was weighed and analyzed for boron, nitrogen, halogens, and magnesium.

Analysis showed:	%B	%N	%Cl	%Br	%Mg	% Remainder
	.23	.35	10.80	47.32	10.73	30.57

Therefore the precipitate consisted primarily of magnesium

halide solvated by ethyl ether.

Reaction of B-trihaloborazenes with Grignard Reagents

Reaction of N-trimethyl-B-trichloroborazene with ethyl magnesium bromide

Into a two-necked flask were placed 25 grams (1.11 moles) of N-trimethyl-B-trichloroborazene, 75 ml. of ethyl ether, a crystal of iodine, a magnetic stirring bar, and 9 grams (.37 moles) of magnesium. The center neck was fitted with an efficient water condenser topped by a dry-ice condenser vented to the air through a drierite tube. A dropping funnel containing 40 grams (.365 moles) of ethyl bromide was placed in the side neck. One ml. of ethyl bromide was added, and if the reaction did not start spontaneously the flask was warmed gently to start the reaction. After the reaction was started, ethyl bromide was added slowly from a dropping funnel, with stirring, at a rate that produced a moderate reflux of the ethyl ether. A white precipitate of magnesium halide formed almost immediately and continued to form throughout the course of the reaction. Addition of ethyl bromide required about two hours. After the addition of ethyl bromide was complete the mixture was refluxed for three or four more hours to complete the reaction. The mixture was filtered through a fritted disc Buchner funnel. The precipitate was washed

several times with ethyl ether, the washings being combined with the filtrate. The combined filtrate and washings were transferred to a flask and the solvent removed at reduced pressure. The flask was then placed in a fractionation apparatus and the product, which was a colorless liquid, was distilled at reduced pressure. The yield of purified N-trimethyl-B-triethylborazene was about 65 per cent.

Analysis showed:	%B	%N	%Cl
Found	15.86	19.45	0.6
Calculated for $B_3(C_2H_5)_3N_3(CH_3)_3$	15.70	20.33	0.00

The boiling point was 82° C. (.65 mm. Hg) and 98° C. (1.8 mm. Hg). The melting point was 1 to 2° C. The refractive index at 22.5° C. was 1.4791.

Reaction of N-trimethyl-B-trichloroborazene with n-butyl magnesium bromide

The same procedure as outlined above for the preparation of N-trimethyl-B-triethylborazene was used for this reaction. In the reaction 22.3 grams (.0987 moles) of N-trimethyl-B-trichloroborazene, 7.2 grams (.30 moles) of magnesium, and 40.6 grams (.296 moles) of n-butyl bromide were used. After fractionation at reduced pressure 21.2 grams of a colorless liquid were obtained. This was a yield of 74 per cent.

Analysis showed:	%B	%N	%Cl
Found	10.92	13.73	0.00
Calculated for $B_3(C_4H_9)_3N_3(CH_3)_3$	11.16	14.45	0.00

The boiling point was 140° C. (1.1 mm. Hg), and the freezing point was -18° to -17°. The refractive index at 22.5° C. was 1.4759.

Reaction of N-trimethyl-B-trichloroborazene with less than the theoretical quantities of Grignard reagent

Less than three moles of Grignard reagent for each mole of N-trimethyl-B-trichloroborazene was used for this reaction. A solution of n-butyl magnesium bromide in ethyl ether was prepared by the reaction of magnesium with 40 grams (.29 moles) of n-butyl bromide. A solution of N-trimethyl-B-trichloroborazene in benzene was placed in a two-necked flask equipped with a water condenser topped with a dry-ice condenser vented to the atmosphere with a drierite column. A dropping funnel containing the n-butyl magnesium bromide was placed in the side neck. With the stirring of the flask contents the n-butyl magnesium bromide was added slowly to the flask. The flask became hot, because the reaction is exothermic. The rate of addition was set so that the n-butyl magnesium bromide was uniformly dispersed in the mixture, and required about a half hour. After addition of n-butyl magnesium bromide was completed, the mixture was

refluxed for about four hours to insure complete reaction. The flask's contents were filtered through a Buchner fritted disc funnel, and washed with ethyl ether as before. The solvent was removed at reduced pressure and the liquid residue placed in a vacuum fractionation apparatus. The liquid was fractionated to give 45 per cent N-trimethyl-B-tri-(n-butyl)-borazene, 35 per cent N-trimethyl-B-di-(n-butyl)-B-chloroborazene, and 20 per cent N-trimethyl-B-(n-butyl)-B-dichloroborazene. The overall yield of borazene derivatives was approximately 75 per cent.

The boiling point of N-trimethyl-B-di-(n-butyl)-B-chloroborazene was 122° C. (1.13 mm. Hg), and its refractive index at 22.5° C. was 1.4807.

Analysis showed:	%B	%N	%Cl
Found	12.19	15.22	12.73
Calculated for $B_3(C_4H_9)_2ClN_3(CH_3)_3$	12.05	15.61	13.17

The boiling point of N-trimethyl-B-(n-butyl)-B-dichloroborazene was 101° C. (1.1 mm. Hg), its freezing point was -4 to -6° C., and its refractive index at 22.5° C. was 1.4876.

Analysis showed:	%B	%N	%Cl
Found	13.04	16.53	27.61
Calculated for $B_3C_4H_9Cl_2N_3(CH_3)_3$	13.11	16.91	28.05

Attempts were made to prepare N-trimethyl-B-diethyl-B-chloroborazene and N-trimethyl-B-ethyl-B-dichloroborazene in the same manner as described above. After sublimation of unreacted N-trimethyl-B-trichloroborazene the remaining liquid was fractionated in an efficient column. In no case was it possible to isolate a fraction that corresponded to a definite composition. On prolonged refluxing or repeated fractionation, N-trimethyl-B-trichloroborazene was obtained. Elemental analysis of the distillate was consistent with mixtures of partially alkylated derivatives. For example, a sample which distilled at 83.5° C. (1.42 mm. Hg) was analyzed for boron and chlorine.

Analysis showed:	%B	%Cl
Found	14.93	28.34
Calculated for $B_3C_2H_5Cl_2N_3(CH_3)_3$	14.79	32.30
Calculated for $B_3(C_2H_5)_2ClN_3(CH_3)_3$	15.23	16.63

Similarly, a sample distilling at 85° C. (1.45 mm. Hg) gave 25.4 per cent chlorine. These analyses indicate that the samples were a mixture of the desired products.

Reaction of N-trimethyl-B-trichloroborazene with allyl magnesium bromide.

The presence of N-trimethyl-B-trichloroborazene apparently made it impossible to start the formation of allyl magnesium bromide. The formation of Grignard reagent from

allyl bromide and magnesium was not successful in the presence of N-trimethyl-B-trichloroborazene. It was necessary first to form the Grignard reagent from magnesium and allyl bromide in ethyl ether and to add it slowly to a solution of N-trimethyl-B-trichloroborazene in ethyl ether. Allyl magnesium bromide was prepared from the reaction of 60 grams (.50 moles) of allyl bromide and 14.6 grams (.58 moles) of magnesium in ethyl ether. A solution of 30 grams (.133 moles) of N-trimethyl-B-trichloroborazene in ethyl ether was placed in a two-necked flask fitted with a reflux condenser topped with a dry-ice condenser vented to the atmosphere through a drierite column. The allyl magnesium bromide was added slowly from a dropping funnel fitted into the second neck. The mixture was then handled as in previous cases. The N-trimethyl-B-triallylborazene was distilled at reduced pressure as a colorless liquid in about 50 per cent yield. Its boiling point was 110 to 112° C. (1.3 mm. Hg), its freezing point was -37 to -39° C., and its refractive index at 22.5° C. was 1.5047.

Analysis showed:	%B	%N	%Cl
Found	13.32	16.66	0.00
Calculated for $B_3(C_3H_5)_3N_3(CH_3)_3$	13.37	17.31	0.00

Reaction of N-trimethyl-B-di-(n-butyl)-B-chloroborazene with 1,4-dichlorobutane and magnesium

Into a 100 ml. flask were placed 5.6 grams (.021

moles) of N-trimethyl-B-di-(n-butyl)-B-chloroborazene, 1.4 grams (.011 moles) of 1,4-dichlorobutane and .62 grams (.0255 moles) of magnesium, and 50 ml. of ethyl ether. The reaction did not start spontaneously, nor was it induced by a crystal of iodine. A few drops of n-butyl bromide was added, and a reaction started immediately but soon ceased. External heating over a period of several hours caused the formation of a white precipitate. The mixture was then filtered and the precipitate washed with ethyl ether. The solvent was removed from the combined filtrate and washings at reduced pressure. A small amount of liquid distilled at a bath temperature of 170 to 200° C. This corresponded to either unreacted starting material or N-trimethyl-B-tri-(n-butyl)-borazene. At a bath temperature of 240° C., liquid again started to distill. No attempt was made to distill this fraction, but the flask was removed from the bath and cooled. The contents of the flask were dissolved in a few ml. of ethyl ether and filtered. Brownish amorphous material remained on the filter, the filtrate being light yellow. The ethyl ether was removed at reduced pressure, leaving a white crystalline solid melting from 65 to 85° C. This liquid distilled at a bath temperature of 275 to 300° C. at .2 mm. Hg. Cryoscopic measurements made with a platinum resistance thermometer, and using cyclohexane dried with calcium hydride as the solvent, gave a molecular weight of 489.

The calculated value for 1,4-di-(N-trimethyl-B-di-n-butyl-borazene) butane is 523.74.

Analysis showed:	%B	%N
Found	12.28	15.51
Calculated for $B_6N_6C_{26}H_{56}$	12.39	16.05

Reaction of N-trimethyl-B-trichloroborazene with 1,4-dichlorobutane and magnesium in ethyl ether

For each mole of N-trimethyl-B-trichloroborazene, 1.5 moles of magnesium and 1,4-dichlorobutane were used. This should presumably lead to crosslinking of the borazene rings with tetramethylene groups. To 16 grams (.071 moles) of N-trimethyl-B-trichloroborazene in a 250 ml. flask were added 125 ml. of ethyl ether and 5.1 grams (.21 moles) of magnesium. Then 13 grams (.102 moles) of 1,4-dichlorobutane were added slowly from a dropping funnel. A slow reaction started. By external heating the mixture was refluxed for eight hours. Upon standing overnight, some of the precipitate turned to a resinous solid. This solid was not decomposed by standing in water and was only slightly affected by standing for one hour in 50 per cent sulfuric acid at room temperature. Very little of the solid material was soluble in ethyl ether, and only a very small amount of this was volatile even at 250° C. and .75 mm. Hg. Some of the hard resinous material was extracted by benzene in a Soxhlet extractor. Analysis for boron and chlorine

showed that the extractable solid had about 1.5 moles of chloride for each borazene ring. This indicated that about one-half of the boron sites are used for chain formation. This is the case if the average chain length is four. If we have a chain of n borazene rings we will have 3n boron atoms and (n + 2) chlorine atoms. Therefore 3n/n + 2 is equal to the experimental ratio of boron equivalents to chlorine equivalents. Since an experimental ratio of two borons to one chlorine was found, substitution in the formula above gives us an average value of four.

In one instance N-trimethyl-B-trichloroborazene was reacted with 1,4-dibromobenzene and magnesium in the presence of ethyl ether. A soft powdery solid, easily decomposed by water, was obtained. This solid dissolved exothermically in dimethylformamide.

Reaction of B-tribromoborazene with ethyl magnesium bromide

Since B-tribromoborazene reacts spontaneously with magnesium, the Grignard reagent could not be prepared in situ as was done previously. The Grignard reagent was prepared by reacting 22.9 grams (.208 moles) of ethyl bromide with 5.1 grams (.210 moles) of magnesium in 50 ml. of ethyl ether. The ethyl magnesium bromide thus prepared was added slowly from a dropping funnel to a solution of 20 grams (.063 moles) of B-tribromoborazene in ethyl ether in a two-necked 250 ml.

flask fitted with a water condenser topped with a dry-ice condenser vented to the atmosphere through a drierite column. A slightly exothermic reaction occurred. Two layers separated during the course of the reaction, indicating that the etherate of magnesium bromide had been formed (27). The top layer was colorless and clear, and the bottom layer was gray and cloudy. The two layers were separated in a separatory funnel and the solvent removed from each layer under reduced pressure. About .07 mole of ethyl bromide was recovered from the solvent. It was identified by formation of the Grignard reagent, addition of dry-ice, and then acidification to liberate the free acid which was titrated with standard sodium hydroxide. The residue from the top layer gave a small amount of liquid condensing at 1 mm. Hg at room temperature. Analysis showed that the liquid contained 9.73 per cent boron and 10.49 per cent nitrogen. The sample was redistilled at atmospheric pressure. Some ethyl ether was recovered at 35° C. The bulk of the liquid boiled at 110 to 116° C. at atmospheric pressure. Upon analysis this sample showed 10.02 per cent boron and 10.84 per cent nitrogen. The infrared spectrum was very similar to the infrared spectrum of the compound produced from the reaction of B-trichloroborazene with ethyl magnesium bromide. The bottom layer upon pyrolysis gave a small amount of liquid whose infrared spectrum corresponded to the infrared spectra of the pyrolysis products previously mentioned in the reaction of mag-

nesium with B-tribromoborazene in ethyl ether.

Reaction of B-tribromoborazene with n-butyl magnesium bromide

Less than three moles of Grignard reagent per mole of B-tribromoborazene were used in an attempt to prepare unsymmetrically-substituted B-(n-butyl)-B-bromoborazene. A solution of n-butyl magnesium bromide was prepared from the reaction of 15.5 grams (.113 moles) of n-butyl bromide with 2.7 grams (.111 moles) of magnesium in ethyl ether. The n-butyl magnesium bromide was added slowly from a dropping funnel to a solution of 18 grams (.057 moles) of B-tribromoborazene in ethyl ether in a 250 ml. two-necked flask fitted with a reflux condenser vented to the atmosphere through a drierite column. A slightly exothermic reaction occurred with the formation of two layers. The layers were separated and the solvent removed from the top layer at reduced pressure. There remained a liquid which distilled at 91 to 93° C. (.33 mm. Hg). The yield was 3.5 grams. Assuming that the product was B-tri-(n-butyl)-borazene, this was a yield of 37 per cent based upon the quantity of Grignard reagent used, and 24 per cent based upon the quantity of B-tribromoborazene used.

Analysis showed:	%B	%N
Found	13.5	17.50
Calculated for $B_3(C_4H_9)_3N_3H_3$	13.04	16.89

The analyses for both both boron and nitrogen are high. The temperature used for the distillation was sufficiently high to cause cleavage of ethyl ether, if any were present. Cleavage of ethyl ether could place ethyl or ethoxy groups on the boron in the borazene ring. This would lower the molecular weight of the compound formed and raise the boron and nitrogen content.

Reaction of B-trichloroborazene with Sodium Ethylate

At one time B-triethoxyborazene was considered to be a possible compound formed from the pyrolysis of the product formed from the reaction of magnesium with B-tribromoborazene in ethyl ether. To prepare B-triethoxyborazene the reaction of sodium ethylate with a solution of B-trichloroborazene was used (2).

Sodium ethylate was prepared by slowly adding absolute ethanol to metallic sodium. In order to obtain complete reaction it was necessary to add sufficient ethanol to dissolve completely the sodium ethylate formed. After the reaction was complete, the excess ethanol was removed at reduced pressure. To remove the excess ethanol, the flask was heated in an oil bath for two hours at 80° C. at reduced

pressure. Analysis showed that the solid obtained had .01452 equivalents / gram of base, as compared to a calculated value of .01469 equivalents / gram.

To a two-necked 250 ml. flask were added 125 ml. of dry benzene and 21.03 grams (.114 moles) of B-trichloroborazene. The other neck was fitted with a solids addition tube containing 23.4 grams (.314 moles) of sodium ethylate. The sodium ethylate was added slowly, by rotation of the addition tube, over a period of two hours with the mixture stirred by a magnetic stirrer. The mixture was refluxed for ten hours after addition of sodium ethylate was complete. The reaction mixture was filtered and the precipitate washed with ethyl ether. The solvent was removed from the combined filtrate and washings at reduced pressure. The remaining liquid was distilled through a small column. The product solidified in the receivers. The distillation temperature was 78° C. (.1 mm. Hg).

Analysis showed:	%B	%N	%C	%H	%O
Found	15.17	19.69	33.85	8.43	22.86
Calculated for $B_3(OC_2H_5)_3N_3H_3$	15.26	19.76	33.88	8.53	22.57

(the oxygen content was found by difference)

Attempted Syntheses for B-monobromoborazenes

To further elucidate the course of the reaction between B-tribromoborazene and magnesium, the preparation of

B-monobromoborazenes was attempted. One possible course of this reaction is a Wurtz-type coupling of borazene rings. Since B-tribromoborazene is trifunctional, this could lead to a complex polymer. If a monofunctional B-monobromoborazene were used in the reaction the end product would be a dimer, which could easily be evaluated. Since reactions of the Grignard reagent with B-tribromoborazene gave low yields and no partially-substituted borazenes, it was not felt that this reaction would be a feasible one for the preparation.

One approach used an attempted bromination of B-chloroborazene or B-alkylborazene linkages with boron tribromide. It was hoped that reactions represented by the following equations would occur:

$$3B_3R_2ClN_3H_3 + BBr_3 \longrightarrow 3B_3R_2BrN_3H_3 + BCl_3$$

$$3B_3R_3N_3H_3 + BBr_3 \longrightarrow 3B_3R_2BrN_3H_3 + 3RBr$$

The reaction of B-trichloroborazene with less than three moles of ethyl magnesium bromide for each mole of B-trichloroborazene was used to prepare a mixture of B-chloro-B-ethylborazenes and B-triethylborazene. No attempt was made to separate this mixture. The mixture of borazenes was then heated with boron tribromide dissolved in benzene at slightly less than the reflux temperature of the mixture, for eight hours. There was extensive decomposition and no products were isolated. Apparently the borazenes present are unstable under these conditions.

The next attempt was based upon the tendency, reported elsewhere in this paper, of borazene compounds to disproportionate. A mixture of B-tribromoborazene and B-triethylborazene, prepared from the reaction of ethyl magnesium bromide with B-trichloroborazene, was heated in an oil bath at 100° C. for an eight-hour period in the hope of producing by disproportionation a mixture of the unsymmetrical compounds. The desired reaction was:

$$B_3(C_2H_5)_3N_3H_3 + B_3Br_3N_3H_3 \longrightarrow B_3(C_2H_5)_2BrN_3H_3 + B_3C_2H_5Br_2N_3H_3$$

However, at the end of this period only B-triethylborazene was isolated, and no B-tribromoborazene or B-bromo-B-ethylborazene could be recovered.

The next procedure tried was the partial reduction of B-tribromoborazene with lithium borohydride (24) according to the equation:

$$2LiBH_4 + B_3Br_3N_3H_3 \longrightarrow B_2H_6 + 2LiBr + B_3BrH_2N_3H_3$$

A solution of 38 grams (.120 moles) of B-tribromoborazene in ethyl ether was prepared in a 250 ml. two-necked flask. The center neck was fitted with a reflux condenser, and a solids addition tube containing 4.5 grams (.206 moles) of lithium borohydride was placed in the side neck after the system was flushed thoroughly with dry nitrogen. Then lithium borohydride was added slowly to the system. A very

vigorous reaction took place. Addition of the lithium borohydride required ten hours. After the reaction was complete the ether was distilled at atmospheric pressure. The borazene derivatives were then removed at reduced pressure. The distillate contained no halogen, so partially substituted B-bromoborazenes were not produced.

A reduction using lithium aluminum hydride (24) was tried according to the equation:

$$2B_3Br_3N_3H_3 + LiAlH_4 \longrightarrow LiBr + AlBr_3 + 2B_3BrH_2N_3H_3$$

Into a 250 ml. two-necked flask were placed 26 grams (.082 moles) of B-tribromoborazene and 1.30 grams (.0344 moles) of lithium aluminum hydride. The center neck of the flask was fitted with a reflux condenser vented to the atmosphere through a drierite column. The side neck was fitted with a dropping funnel containing 125 ml. of ethyl ether. After the system was flushed with nitrogen, ethyl ether was added. A vigorous reaction took place. The reaction was continued for fifteen hours. Then the ethyl ether was removed by distillation at atmospheric pressure. After removal of solvent was complete the flask was evacuated, but no borazenes were recovered, even by heating the flask to 100° C. in an oil bath.

Reaction of B-tribromoborazene with Tetrahydrofuran

An attempt to react B-tribromoborazene with magnesium in the presence of tetrahydrofuran, dried with calcium hydride, failed because of an exothermic reaction between tetrahydrofuran and B-tribromoborazene. This reaction took place with pure tetrahydrofuran, with tetrahydrofuran dissolved in benzene, and with tetrahydrofuran dissolved in ethyl ether. A solution of 13.94 grams (.044 moles) of B-tribromoborazene was prepared in dry ethyl ether. Then tetrahydrofuran was added slowly from a dropping funnel. After the reaction seemed complete a 5 ml. excess was added. The solvent and excess tetrahydrofuran were removed by keeping the flask at .1 mm. Hg at room temperature until it had reached a constant weight. This required about twenty hours. It was found that 9.36 grams (.130 moles) of tetrahydrofuran had been taken up. This gives a ratio of 1 mole of B-tribromoborazene to 2.95 moles of tetrahydrofuran. Since a small amount of material was lost during removal of solvent, it is probable that the true ratio is one to three. The product of the above reaction was a white solid which was soluble in excess tetrahydrofuran.

The product of the above reaction could be decomposed upon heating to 250° C. at 1 mm. Hg to give a liquid with a boiling point range from 65 to 160° C. (.4 mm. Hg). It seems probable that this liquid product consists of B-sub-

stituted borazenes formed from ether cleavage resulting from the pyrolysis of the addition product between B-tribromoborazene and tetrahydrofuran.

General Techniques

The samples were analyzed by hydrolysis to boric acid, ammonia or the amine, and halogen ion, if present. The acid-base titrations were made using a Beckmann Model G pH meter.

Hydrolysis of the B-haloborazenes was effectively accomplished by addition of water and refluxing for a short period. A water trap was placed at the condenser outlet to prevent the loss of hydrogen halide, amine, or ammonia. Hydrolysis of the B-haloborazenes gives a very slightly acidic solution.

Hydrolysis of the B-alkylborazenes or the B-allylborazenes was effected by boiling in 20 per cent sulfuric acid for a half hour, then adding 30 per cent hydrogen peroxide and refluxing for another two hours to oxidize to boric acid the alkyl boronic acid (29) produced. A water trap was placed at the condenser outlet as before. Basic hydrolysis was not used because of the danger of contaminating the solution with boron from the glassware.

Mixtures containing magnesium were hydrolyzed as described above for B-alkylborazenes.

Boric acid was determined by first titrating the solution with standard sodium hydroxide to the first strong break in the titration curve, usually occurring at a pH of 5 to 6, then adding mannitol in large excess and titrating to the first break. The difference in volumes between the two endpoints represented the boric acid content of the sample, the mannitol complex of boric acid being monobasic. This procedure was satisfactory in the presence of methylamine, or ammonia. The sharpness of the endpoint is reduced slightly in the presence of methylamine and is reduced considerably in the presence of ammonia.

Ammonia or methylamine was determined by distillation from a basic solution into boric acid. The boric acid solution of ammonia or methylamine may then be titrated directly with standard hydrochloric acid. Since excess boric acid buffers the solution and reduces the sharpness of the endpoint, a minimum quantity of boric acid was used.

Halogen was determined by the Volhard method. To the acidified sample was added a slight excess of standard silver nitrate, as judged by coagulation of the precipitate at the endpoint. Then 1 ml. of ferric ammonium sulfate solution was added as an indicator, and if chloride was to be determined, 4 to 5 ml. of nitrobenzene were used. The mixture was then titrated to the ferric thiocyanate

endpoint with standard potassium thiocyanate solution. The difference between the titers is equivalent to the halogen content of the sample. Mixtures of bromide and chloride ions were determined by potentiometric titration using a glass electrode as the reference electrode and a silver electrode for the indicator electrode, and the Beckmann Model G pH meter as the potentiometer.

Magnesium was determined gravimetrically by precipitation with 8-hydroxyquinoline and weighing of the dihydrate dried at 105° C.

In general, all transfers, filtrations, and other operations which would have involved the exposure of the borazene compounds to atmospheric moisture were carried out in a dry box. In a few cases, such as the determination of the refractive indices, transfers were made by flushing the immediate area with nitrogen which was dried by passing cylinder nitrogen through sulfuric acid and then magnesium perchlorate. Determination of the infrared spectra was made on solutions that had been prepared and placed in a hypodermic syringe in the dry box. The hypodermic syringe was quickly transferred to the infrared cell in the instrument room where the relative humidity was low. In the case of B-tribromoborazene and B-trichloroborazene the infrared cell was filled in the dry box. It was necessary to clean the syringes immediately after use to prevent them

from becoming frozen.

The refractive indices were determined with an Abbe refractometer.

Carbon tetrachloride, used as a solvent for the samples in obtaining the infrared spectra, was dried with calcium hydride. Immediately before use, the carbon tetrachloride was filtered from the calcium hydride in the dry box.

All the ethyl ether used in this research was Mallinckrodt anhydrous grade and was used as supplied. The ethyl ether cans were opened in the dry box. After being opened the ethyl ether was stored in the dry box.

Commercial chlorobenzene from Dow Chemical Company, reagent grade from Merck, and Fisher Certified grade were all used equally successfully with no further treatment for the preparation of the haloborazenes.

Laboratory grade benzene was stored over calcium hydride and filtered immediately before being used.

The tetrahydrofuran was refluxed with calcium hydride, then distilled and stored over calcium hydride and filtered when needed.

Standard Grignard grade magnesium turnings were used for the Grignard reactions.

The alkyl halides were used as supplied by Columbia Organic Chemicals Company.

The allyl bromide was distilled from calcium sulfate

before use.

Matheson technical grade boron trichloride was used for the preparation of the B-trichloroborazene and N-trimethyl-B-trichloroborazene.

Technical boron tribromide, as supplied by American Potash and Chemical Corporation, was used for the preparation of B-tribromoborazene and N-trimethyl-B-chloro-B-bromoborazene.

INFRARED SPECTRA

The infrared spectra were obtained from solutions of the borazene in carbon tetrachloride. Several spectra were measured in potassium bromide pellets. These spectra were generally not satisfactory because the absorption bands were usually very broad and diffuse. The bands also appeared to be shifted somewhat from their location when determined in carbon tetrachloride solution. The infrared spectra were recorded on a Perkin-Elmer Model 21 double beam spectrophotometer. The spectra shown in the figures were recorded with the solvent in a .209 mm. cell compared to a .206 mm. cell used for the sample, except for the spectra of B-trichloroborazene and B-tribromoborazene for which a .209 mm. cell was used for the solvent and a .215 mm. cell was used for the sample. The speed of the instrument was controlled manually and set at 0 in the regions of absorption maxima.

The figures at the end of this chapter are labeled with the name of the compound. The first figure shows a comparison of the six to eight micron region of N-trimethyl-B-trichloroborazene, N-trimethyl-B-dichloro-B-(n-butyl)-borazene, N-trimethyl-B-chloro-B-di-(n-butyl)-borazene, N-trimethyl-B-tri-(n-butyl)-borazene, N-trimethyl-B-triethylborazene, and N-trimethyl-B-triallylborazene. Figure 2 shows the spectra of B-trichloroborazene and B-tri-

bromoborazene. Figure 3 shows the spectra of N-trimethyl-B-dichloro-B-(n-butyl)-borazene and N-trimethyl-B-chloro-B-di-(n-butyl)-borazene while Figure 4 containes the spectra of N-trimethyl-B-trichloroborazene and 1,4-di-(N-trimethyl-B-chloro-B-di-(n-butyl)-borazene)-butane. Figure 5 has the spectra of N-trimethyl-B-tri-(n-butyl)-borazene and N-trimethyl-B-triethylborazene. Figure 6 contains the spectra of N-trimethyl-B-triallylborazene and B-triethoxyborazene.

In Table 1 there is listed the absorption maxima found for borazenes containing hydrogen on the nitrogen, while Table 2 contains the spectra of the N-trimethylborazenes. The abbreviations used are: vs, very strong; s, strong; ms, medium strong; m, medium; mw, medium weak; and w, weak. The tables list the absorption bands in microns.

The 2.9 micron band found in all the compounds in Table 1 represents a nitrogen-hydrogen stretching frequency. The frequencies at 3.36 and 3.35 microns are carbon-hydrogen stretching bands. The 6.97 and 6.92 micron peaks found for B-tribromoborazene and B-trichloroborazene, respectively, may be assigned to ring vibration. The absorption maxima at 8.73 microns found for B-triethoxyborazene and for B-diethoxy-B-ethylborazene is the carbon-oxygen band.

TABLE 1

INFRARED ABSORPTION BANDS FOR B-SUBSTITUTED BORAZENES

$B_3N_3H_3Br_3$	$B_3N_3H_3Cl_3$	$B_3N_3H_3(OC_2H_5)_3$	$B_3N_3H_3C_2H_5(OC_2H_5)_2$
2.92 m	2.89 m	2.87 m	2.87 m
		3.36 s	3.35 s
		3.47 ms	3.47 s
6.97 vs	6.92 vs	6.67 vs	6.67 vs
		6.80 vs	6.78 vs
7.24 s	7.27 s	7.19 vs	7.19 vs
		7.33 ms	7.34 m
7.51 m	7.50 m		7.51 w
		7.75 ms	
		8.07 m	
		8.42 s	8.42 vs
		8.73 s	8.73 ms
8.95 m	8.94 m	9.03 m	9.03 m
		9.42 m	
9.74 vs	9.69 vs	9.55 vs	9.55 m
		10.5 w	
14.20 vs	14.23 vs	14.10 vs	14.10-.20 s[a]
		14.30 vs	14.31-.02 vs
14.95 vs			14.40-.50 s[a]

[a]Shoulder

The very strong band found at 14.20 microns for B-tribromoborazene, and at 14.23 microns for B-trichloroborazene may be assigned to nitrogen-hydrogen in plane bending following the assignments of other workers (19). The other compounds listed above also undoubtedly show this mode, but because of the closeness of other vibrations an assignment may not be made. Similarly, it is difficult to assign the 7 micron vibration in these compounds because of the strong carbon to hydrogen bands occurring in the same region. For

the compound N-trimethylborazene, modes occurring at 6.68 and 7.22 microns have been assigned to CH_2 and CH_3 deformations, respectively (19). On the basis of this, one could assign the ring vibration to 6.80 and 6.78 microns for B-triethoxyborazene and B-ethyl-B-diethoxyborazene, respectively. However, this is a somewhat higher frequency than is usually assigned to the ring vibration. The absorption band found at 8.42 microns in B-triethoxyborazene and B-diethoxy-B-ethylborazene is assigned as the boron to oxygen stretching frequency.

The data in Table 2 are for N-trimethyl-B-alkyl, allyl, or chloroborazene. They were furnished through the courtesy of George Ryschkewitsch. The table heading refers to the boron substituent.

The absorption bands found in the 3.4 micron region are the carbon-hydrogen stretching modes. The 6.11 micron band found in the spectra of N-trimethyl-B-triallylborazene is associated with the carbon-carbon double bond. The very strong band found at about 7.1 microns is assigned to the ring vibration. It is seen from Figure 1 that this band splits when the borazene is unsymmetrical. This is similar to the results found when other ring compounds are unsymmetrically substituted. This peak in N-trimethyl-B-triethylborazene has a small peak at 7.283 microns which gives it the appearance of splitting. However, this sample con-

TABLE 2

INFRARED ABSORPTION BANDS FOR N-TRIMETHYL B-SUBSTITUTED BORAZENES

$B_3(C_2H_5)_3$	$B_3(C_3H_5)_3$	$(C_4H_9)_2B_3(CH_2)_4B_3(C_4H_9)_2$
	3.283 m	
3.409 vs	3.443 s	3.45 s
	3.542 s	
	6.110 s	
6.815 vs		
		6.86 vs
6.880 vs	6.893 vs	
7.124 vs	7.139 vs	7.142 vs
7.283 w		
7.570 m	7.579 m	
8.172 ms	8.295 ms	8.27 m
	8.493 ms	8.50 m
9.094 s	9.096 vs	9.10 m
	9.483 -	
9.657 s	9.493 w	9.52 m
9.908 vs	9.980 s	
	10.068 m	
10.262 w		
10.761 w		
	11.125 vs	

Note: These data were furnished through the courtesy of Dr. George E. Ryschkewitsch.

[a]Shoulder

TABLE 2 - Continued

$B_3(C_4H_9)_3$	$B_3Cl(C_4H_9)_2$	$B_3Cl_2C_4H_9$	B_3Cl_3
3.425 s	3.418 s	3.414 s	3.398 s
3.505 m	3.499 s	3.503 s	3.50 s
			5.905 w
			6.022 w
			6.079 w
			6.115 w
	6.800 vs	6.808 vs	
6.850 vs	6.832 vs		6.828 vs
	6.920 vs	6.910 vs	6.878 vs
7.135 vs	7.084 vs	7.102 vs	7.176 vs
7.262 w	7.227 vs	7.231 vs	
7.372 w	7.370 w [a]		
7.474 w	7.465 w	7.467 w	
		7.750 mw	7.792 s
		7.998 w	7.960 m[a]
8.283 w	8.280 w		
8.394 w	8.394 w	8.380 w	
8.50 w	8.485 w	8.487 w	
9.100 s	9.089 ms		
9.229 w	9.261 ms	9.252 s	9.224 s
9.538 m	9.590 -	9.637 ms	
	9.599 ms		
	9.985 -	10.074 ms	
	10.000 w		
	10.280 m	10.272 ms	10.272 s
10.548 w	10.575 w	10.565 w	
11.29 w	11.390 -	11.320 w	
	11.405 w		
		13.950 w	
		14.720 -	14.768 s
		14.750 m	14.908 s
			15.088 s

tained a small amount of chlorine, so the splitting, if real, may be due to the same factor as the splitting for the unsymmetrical B-chloro-B-(n-butyl)-borazenes. An absorption band at 10.27 microns is apparently associated with the chlorine atom. The tables show that its intensity varies from strong in N-trimethyl-B-trichloroborazene, to medium strong for N-trimethyl-B-dichloro-B-(n-butyl)borazene, to medium for N-trimethyl-B-chloro-B-di-(n-butyl)-borazene. This peak is non-existent in the B-trialkylborazenes, except for N-trimethyl-B-triethylborazene. The presence of this band in this compound may be ascribed to the presence of a small amount of chlorine in it. This band falls at a somewhat shorter wave length than is usually associated with the carbon-chlorine stretching frequency, but the boron-chlorine bond in this compound contains some double bond character which could increase the force constant, thus increasing the frequency of vibration and causing this shift. On the same basis the very strong 9.69 micron band found in B-trichloroborazene could be assigned to the same vibration. It can be argued that the double bond character should be greater for B-trichloroborazene than for N-trimethyl-B-trichloroborazene because N-methyl substitution has been found to increase ring resonance, and that therefore the stretching frequency should increase for B-trichloroborazene. However, this would necessitate as-

signing the absorption maxima at 9.74 microns found in B-tribromoborazene to the boron-bromine bond, and it is somewhat difficult to rationalize the appearance of this bond at such a short wave-length.

An absorption band found at approximately 9.25 microns shows a regular change in intensity from strong to weak as one proceeds through the series from N-trimethyl-B-trichloroborazene to N-trimethyl-B-tri-(n-butyl)-borazene. A spectral peak is found close to 9.1 microns in all the compounds containing two or more boron-carbon bonds. On this basis this vibration mode is assigned to the boron-carbon bond. A spectral band is found at about 14.75 microns for N-trimethyl-B-trichloroborazene and N-trimethyl-B-dichloro-B-(n-butyl)-borazene, but in no other case. This band is then associated with the boron-chlorine bond.

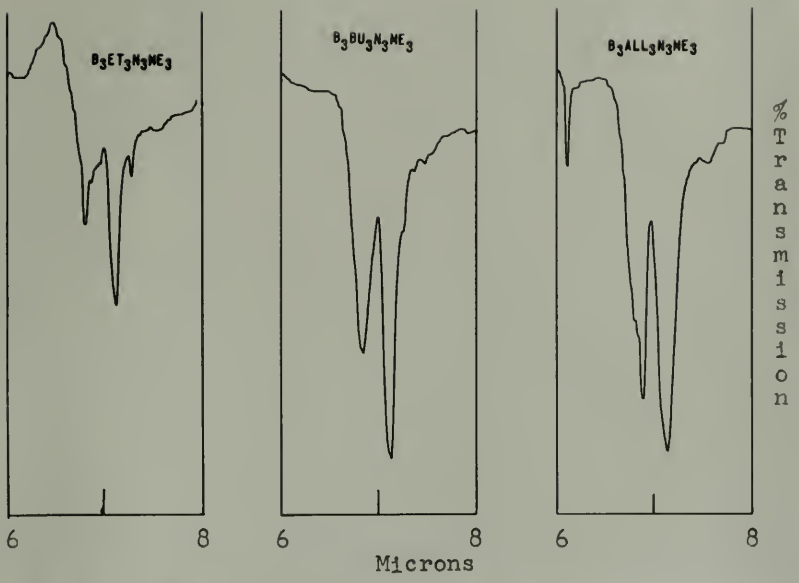
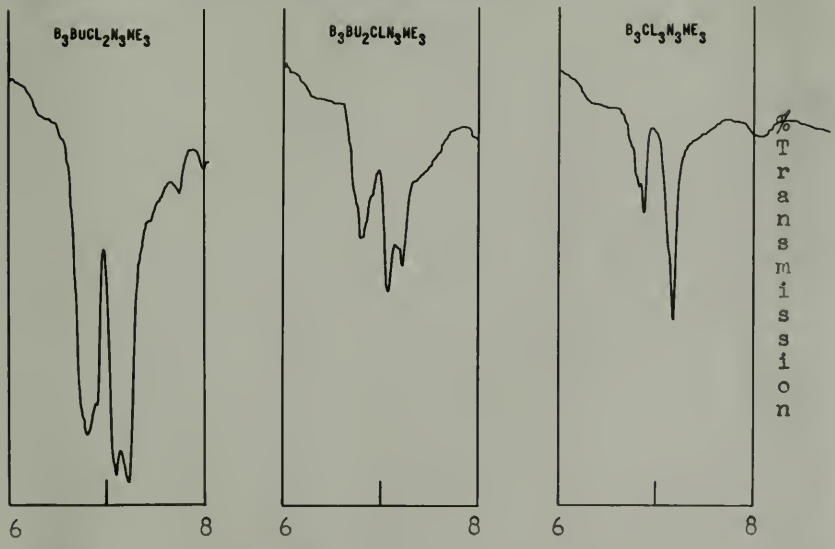


Fig. 1 - Comparison of the Six to Eight Micron Region of N-trimethyl-B-substituted Borazenes



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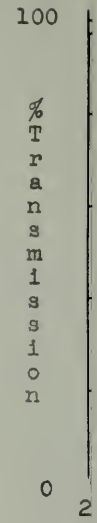

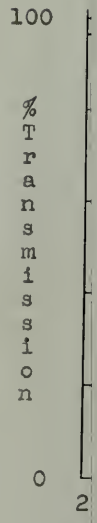

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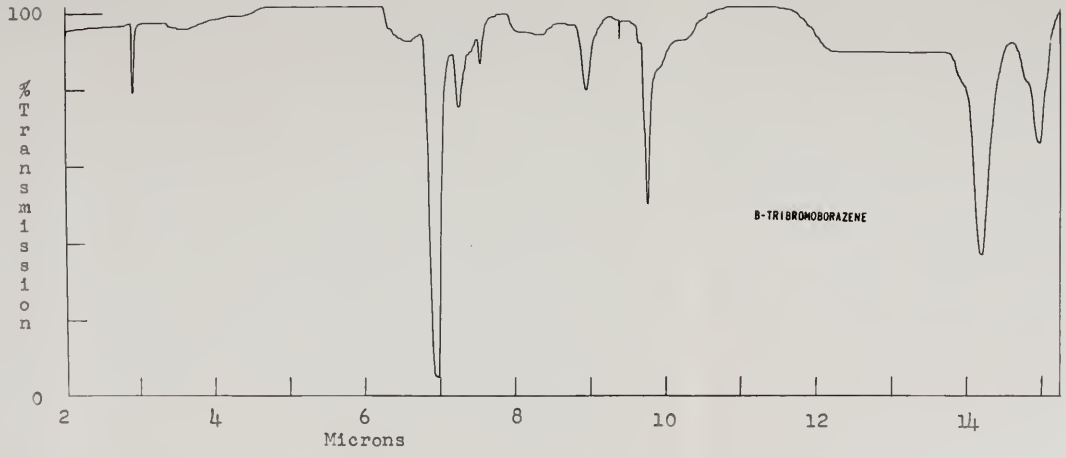


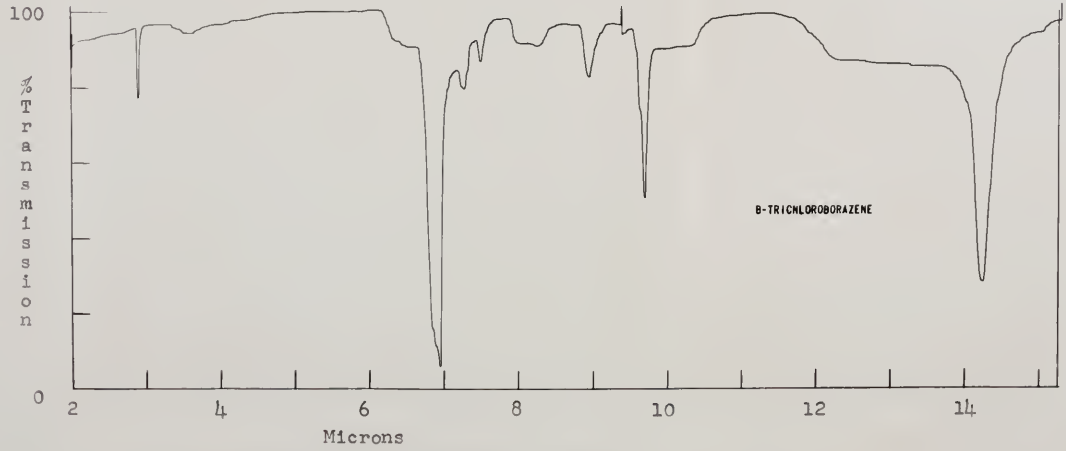


Fig. 2 - Spectra of B-trichloroborazene and B-tribromoborazene

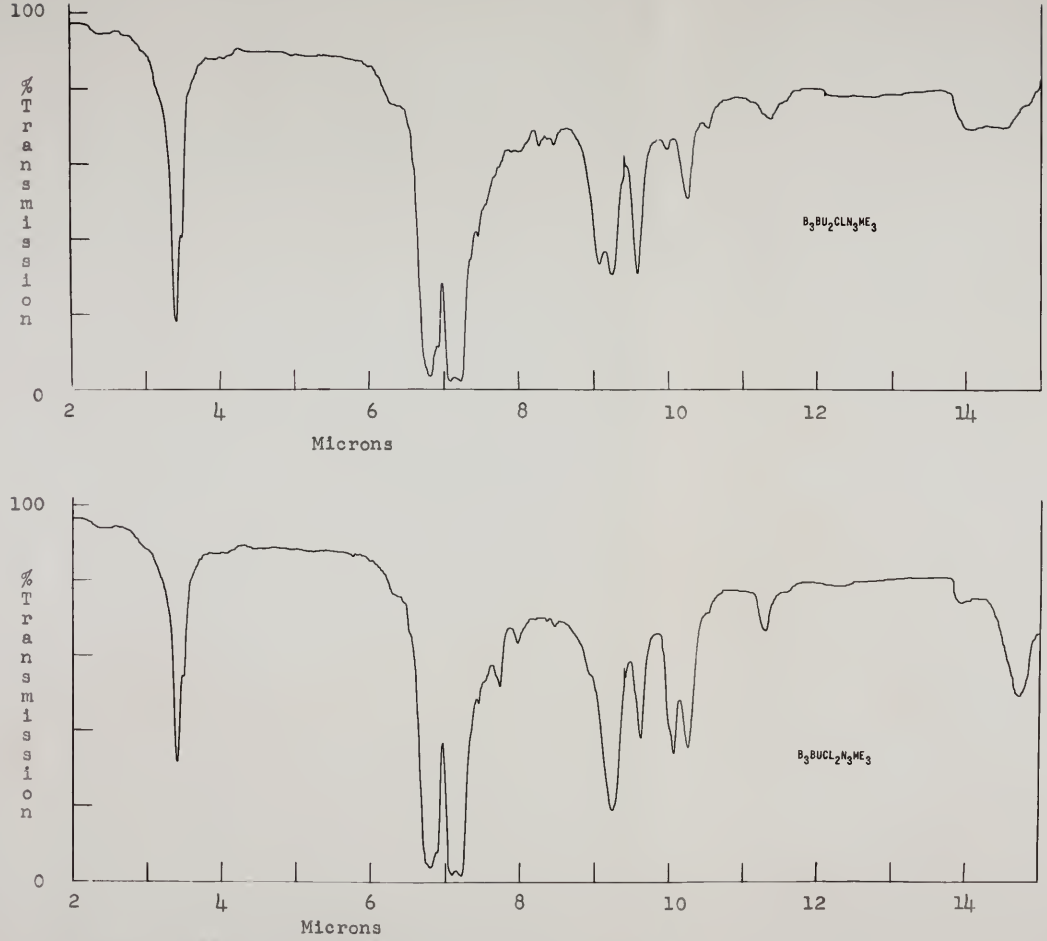
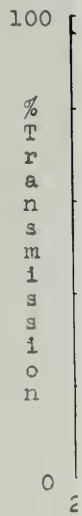
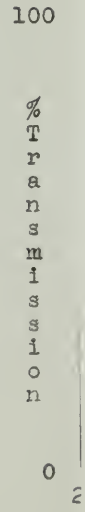


Fig. 3 - Spectra of N-trimethyl-B-dichloro-B-(n-butyl)-borazene and N-trimethyl-B-chloro-B-di-(n-butyl)-borazene





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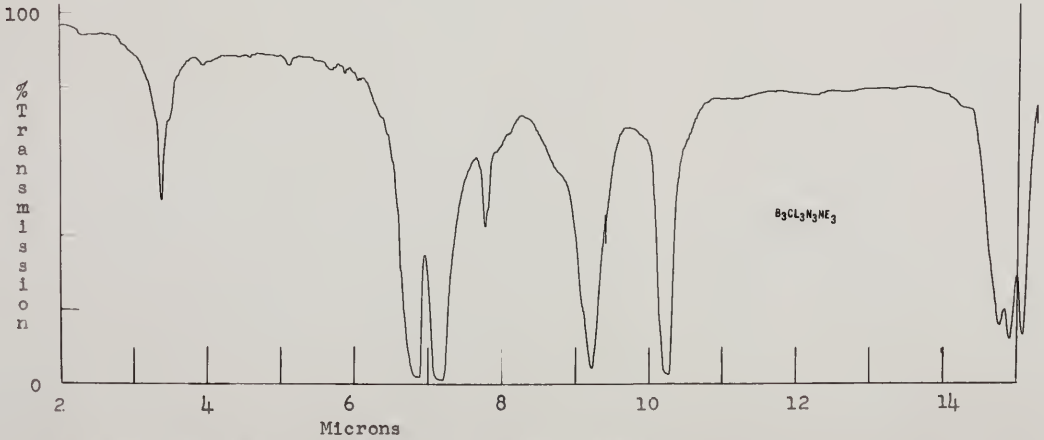


Fig. 4 - Spectra of N-trimethyl-B-trichloroborazene and 1,4-di-(N-trimethyl-B-di-(n-butyl)-borazene) butane

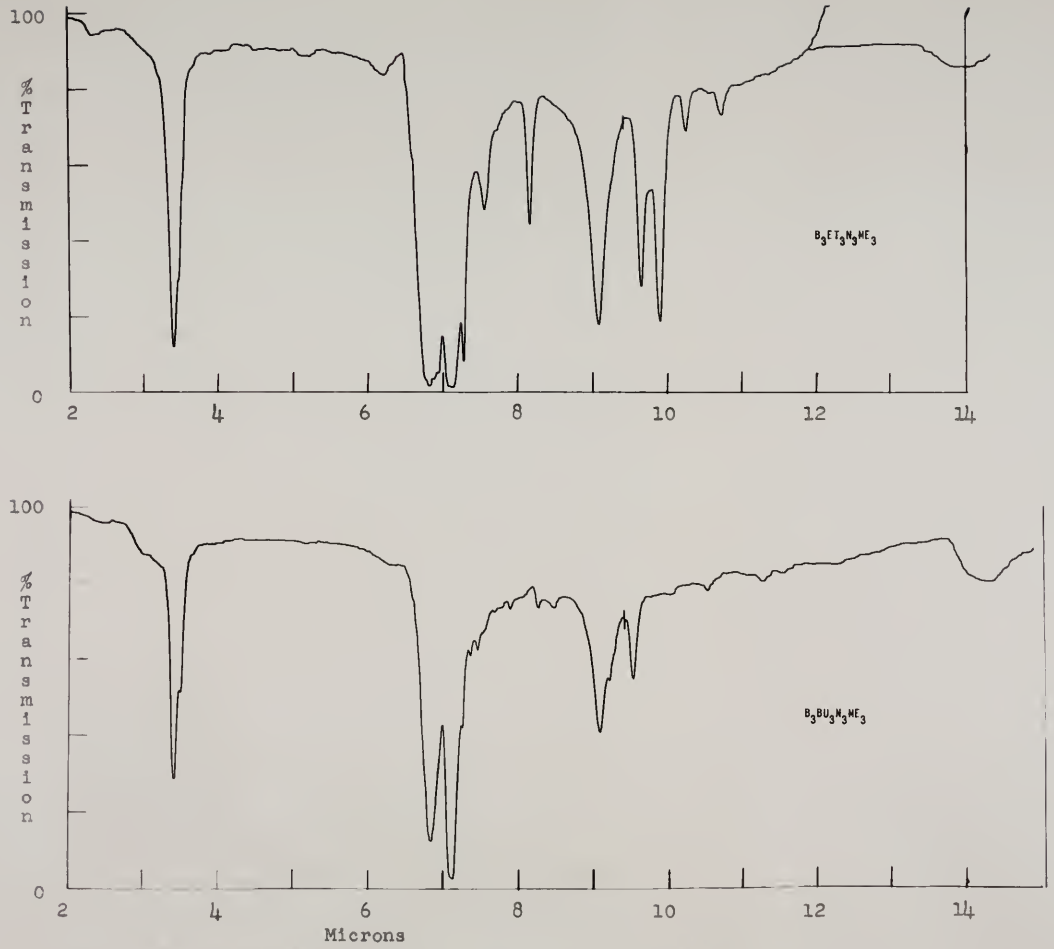
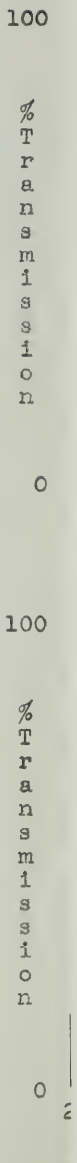


Fig. 5 - Spectra of N-trimethyl-B-tri-(n-butyl)-borazene and N-trimethyl-B-triethylborazene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DISCUSSION

The original purpose of this research, as stated in the Introduction, was the preparation of analogs of organometallic compounds in the borazene system. Because only B-haloborazenes had been prepared, it was necessary to use borazenes in which the boron atoms were substituted with halogen. Using magnesium, a reaction of the following type was sought:

$$B_3X_3N_3R_3 + 3Mg \longrightarrow B_3Mg_3X_3N_3R_3$$

Because Grignard reagents react with compounds containing active hydrogen (12), and the hydrogen on the nitrogen in the borazene ring presumably is active, it was decided to use borazenes in which the hydrogens on the nitrogen had been replaced by methyl groups. No usual Grignard reagent formation was established for N-trimethyl-B-trichloroborazene, the first compound tried, when ethyl ether was the solvent for the reaction. It is known that bromobenzene forms Grignard reagents readily, whereas chlorobenzene forms Grignard reagents with greater difficulty. Proceeding on the analogy with borazene and the benzene system, the next compound tried was N-trimethyl-B-bromo-B-chloroborazene. This compound also failed to show a reaction with magnesium. In a similar manner it was found that B-trichloroborazene failed to form borazene analogs of the Grignard reagent using ethyl ether as the solvent.

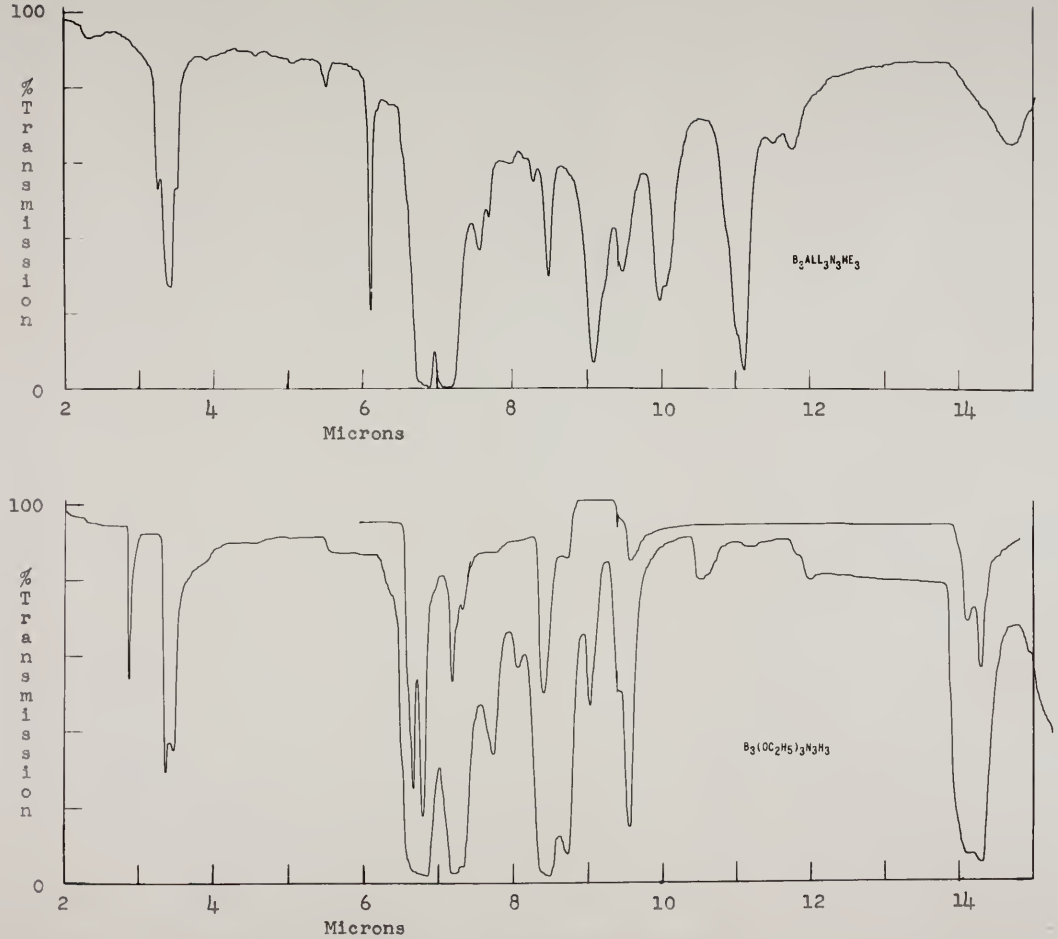


Fig. 6 - Spectra of N-trimethyl-B-triallyl-borazene and B-triethoxyborazene

The next compound tried, B-tribromoborazene, showed a very vigorous reaction with magnesium in ethyl ether. With present data this reaction is somewhat difficult to interpret unequivocally, though several possibilities, none of which are free from objections, can be discussed.

No simple compounds could be isolated from the reaction mixture after removal of the solvent, or by attempted extraction with benzene. As stated in the experimental section, two layers with strikingly different properties were formed during the reaction. Magnesium bromide is known to form a two-layer system with ethyl ether above 22.8° C. (27). The bottom layer consists of a small quantity of ethyl ether dissolved in magnesium bromide dietherate. The top layer is ethyl ether containing a small quantity of magnesium bromide. It was consistently found that only about one-and-one-half moles of magnesium were consumed for each mole of B-tribromoborazene, whereas if there were complete reaction to give a B-tribromomagnesium borazene, there should be three moles of magnesium consumed per mole of borazene.

Elementary analysis showed that the approximate ratio of elements in the vacuum-dried residue from the top layer was $B_3N_3MgBr(Et_2O)_{1.5}$. For the residue from the bottom layer, a ratio of $B_3N_3Mg_3Br_6(Et_2O)_{4.5}$ was found.

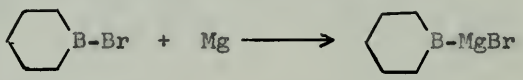
Neither layer seemed to show appreciable reactivity toward methyl iodide, or toward N-trimethyl-B-trichloroborazene. The top layer showed some reactivity toward n-butyl magnesium bromide, probably to give B-n-butyl substitution. This product was not completely evaluated, but the volatility of a fraction of the liquid obtained was considerably less than found for B-tri-(n-butyl)-borazene, indicating a molecular weight considerably in excess of that of B-tri-(n-butyl)-borazene. The solid residue obtained from each of the layers, when pyrolyzed at reduced pressure, gave the same product, B-ethyl-B-diethoxyborazene. If B-tribromoborazene is reacted with magnesium in the presence of an excess of N-trimethyl-B-trichloroborazene, a precipitate of magnesium halide containing a significant amount of chlorine is formed. The mixture obtained from the reaction of magnesium and B-tribromoborazene showed some reactivity toward acetone, to give a liquid product, and toward dry-ice, to give a solid product. The infrared spectra of the ethyl ether solution of the two layers showed no evidence of boron to hydrogen bonds, which usually have high absorption intensities, but showed a nitrogen to hydrogen stretching band. A similar result was obtained from spectra of the solids in potassium bromide pellets.

A possible path for the reaction of B-tribromobor-

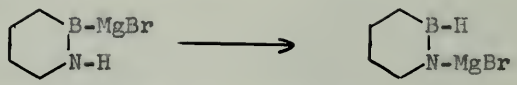
azene with magnesium is the reaction of a Grignard-type reagent with active hydrogen on the borazene nitrogen. Compounds containing active hydrogen, such as pyrrole, react with Grignard reagents with the active hydrogen adding to the organic group to give a hydrocarbon, and the magnesium halide radical linking with the compound originally containing the reactive hydrogen to give a Grignard reagent of the compound (12). For example, methyl magnesium iodide reacts with pyrrole according to the equation:

$$(CHCH)_2NH + CH_3MgI \longrightarrow (CHCH)_2NMgI + CH_4$$

The hydrogen on the nitrogen in borazenes presumably is active, as explained in the Introduction. Therefore we could have the first step in the reaction being the reaction of magnesium with a boron to bromine bond to form a boron to magnesium to bromine bond.



This compound would then react with the active hydrogen on the nitrogen to form a nitrogen to magnesium to bromine bond, and a boron to hydrogen bond.



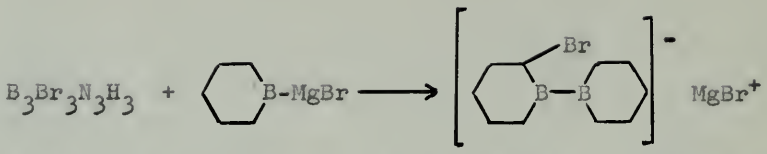
This reaction sequence has been discounted almost completely for a number of reasons. The infrared spectra showed no evidence of any boron to hydrogen stretching frequencies,

but did show the characteristic nitrogen to hydrogen stretching frequency. This reaction sequence also does not satisfactorily explain the reaction of only one-and-one-half moles of magnesium per mole of B-tribromoborazene, except by postulating an equilibrium mixture in which not all of the boron to bromine bonds are reactive toward magnesium. Because substitution at one site seems to have little effect on the reactivity of other sites in borazenes, except for cases involving steric strain which is not applicable here, this postulate does not seem to be reasonable. This hypothesis does not explain the formation of magnesium bromide during the reaction and the analysis found for the layers obtained.

Another possible course of the reaction would be the formation of a tetravalent boron complex. Trialkyl or triarylboron will react with organo-metallic compounds to yield tetracovalent boron complexes (13). For example, tri-(n-butyl)-boron will react with phenyl magnesium bromide according to the following equation (10):

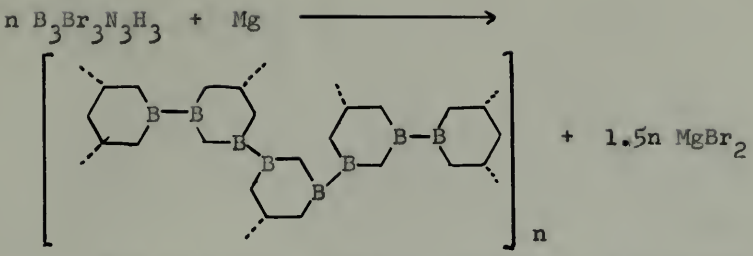
$$B(C_4H_9)_3 + C_6H_5MgBr \longrightarrow (MgBr)^+(C_6H_5B(C_4H_9)_3)^-$$

The first step in this reaction sequence would be the same as previously outlined. The borazene Grignard reagent would then react with another borazene molecule to give a tetravalent boron complex.

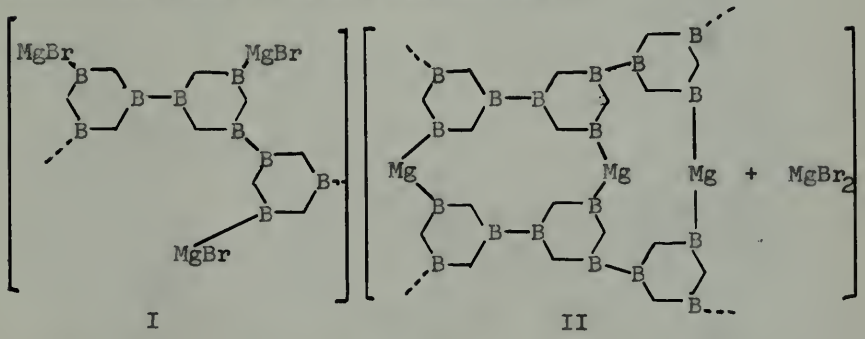


This reaction satisfactorily explains the consumption of one-and-one-half moles of magnesium for each mole of B-tribromoborazene. However, since the above reaction does not involve the formation of magnesium bromide, it can not be the final step of the reaction. It is very possible, however, that it is an intermediate in the hypothesis discussed below.

The next mechanism considered is a Wurtz-type coupling of the borazene rings to give polymeric species. Since the boron to halogen bond has been shown to react with Grignard reagents to give condensation products and magnesium halide, it is conceivable that a Grignard reagent is first formed, and then immediately couples with boron to bromine bonds present in the reaction mixture. This would give rise to a polymeric species of borazene rings linked together with boron to boron bonds between the rings. Since B-tribromoborazene is trifunctional, complete reaction would form a two-dimensional network of borazene rings. A tetracovalent boron complex discussed above could be the intermediate in the reaction. The reaction may be written as:



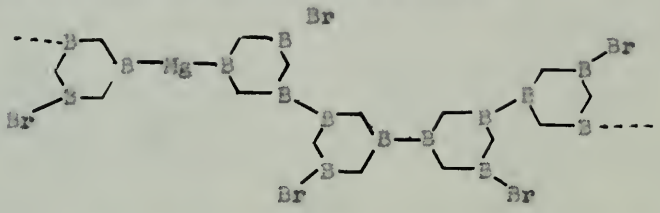
This reaction course reasonably satisfactorily explains the use of only one-and-one-half moles of magnesium for each mole of B-tribromoborazene. From the analytical data the top-layer compound can be postulated as consisting of borazene chains, linked together by boron to boron bonds, with the third boron site on each ring occupied by a magnesium bromide unit. Alternatively, an equilibrium mixture of magnesium bromide and borazene chains linked with magnesium attached to the boron on the borazene ring may be assumed. These possibilities are represented by structures I and II below, respectively.



I II

Because magnesium bromide is somewhat soluble in ethyl

ether, it is possible that the borazene rings in the top layer contain no attached bromine. It is clear from the lack of reactivity of the top layer towards magnesium that any bromine attached to the ring must be attached indirectly through a magnesium atom. This consideration rules out an equilibrium mixture of the type:



For clarity in the following discussion we will assume that B-tribromo-magnesium-borazene is produced and reacts with an approximately equal number of molecules of B-tribromoborazene to give compounds corresponding to the analyses of the two layers. The hypothetical reaction may be written:

$$5B_3Br_3N_3H_3 + 6B_3Mg_3Br_3N_3H_3 \longrightarrow$$

$$4B_3N_3H_3Mg_3Br_6 + 7B_3N_3H_3MgBr$$

(This equation is not exactly balanced, but it must be remembered that the atom ratios are approximate.) Each mole of borazene in the top-layer chain leads to the formation of one mole of magnesium bromide which is found in the bottom-layer etherate. Subtracting seven moles of magnesium bromide from the bottom layer leaves us with

4 $B_3N_3H_3Mg_{1.25}Br_{2.5}$. Complete cross-linking of the borazene units would lead to a ratio of $B_3N_3H_3Mg_{1.5}Br_3$. From present data, therefore, we can conclude that the borazene in the bottom layer is in substantially the same form as the borazene present in the top layer. This is in accord with the similarity of the infrared spectra obtained from the potassium bromide pellets of the solids from both layers. Formation of identical pyrolysis products by both layers also indicates a similarity in the borazene present in each of the layers.

A possible objection to the above hypothesis lies in the assumption of boron to magnesium to bromine bonds, because these units should have coupled with other boron to bromine bonds during the course of the reaction. However, unless we make the postulation that the coupling reaction is very much faster than the Grignard reagent formation reaction, there should be formation of an excess of Grignard reagent linkages over unreacted boron to bromine bonds. These linkages can not, of course, couple to form boron to boron bonds, though they can react to form boron to magnesium to boron bonds, and magnesium bromide, in an equilibrium mixture. This reaction sequence will, of course, require the consumption of somewhat more than one-and-one-half moles of magnesium for each mole of B-tribromoborazene, as was written in the hypothetical equation

above. This could be true within experimental error. Alternatively, the assumption could be made that some of the boron to bromine bonds are buried in the polymer and become unavailable for reaction.

The reaction of magnesium with B-tribromoborazene in the presence of N-trimethyl-B-trichloroborazene seems to furnish indirect evidence for the formation of a boron to magnesium to bromine bond. The formation of a precipitate containing chlorine was observed. Since N-trimethyl-B-trichloroborazene does not react with magnesium under these conditions, the N-trimethyl-B-trichloroborazene must have reacted with one of the products of the reaction between magnesium and B-tribromoborazene. Since N-trimethyl-B-trichloroborazene couples with Grignard reagents, it could react with a Grignard reagent formed from magnesium and B-tribromoborazene to give magnesium bromide chloride, and borazene molecules linked between boron atoms according to the equation:

$$B_3Cl_3N_3(CH_3)_3 + B_3Br_3N_3H_3 + Mg \longrightarrow MgClBr + N_3H_3B_3Br_2\text{-}B_3Cl_2N_3(CH_3)_3$$

An alternate hypothesis would be an exchange of chlorine for bromine between magnesium bromide and N-trimethyl-B-trichloroborazene. The former possibility seems to be the more likely one. The ratio of bromine to chlorine in the

precipitate indicates that the Grignard reagent, if formed, reacts with B-tribromoborazene at a greater rate than it reacts with N-trimethyl-B-trichloroborazene.

There is little evidence concerning the chain length of the hypothetical polymer. Since the top layer is not viscous, the molecular weight must be relatively low. The insolubility of the solid obtained from the top layer in benzene furnishes evidence of boron to magnesium bonds, because normally the borazenes are as soluble in benzene as in ethers. The bottom layer was very viscous, but this in itself can not be used as an indication of a high molecular weight unit, since the bottom layer contains a large amount of the dietherate of magnesium bromide (27).

Another possibility is the elimination of hydrogen with condensation of the rings into a boron nitride structure. The reaction sequence could take the form of elimination of hydrogen bromide followed by condensation of the rings through boron to nitrogen bonds. The hydrogen bromide eliminated reacts with magnesium to form magnesium bromide. The presence of a nitrogen to hydrogen stretching frequency in the infrared spectrum would seem to preclude the existence of this type of structure as the major component of the system. In addition, such a structure would almost certainly be insoluble. The present evidence can not exclude the presence of small amounts of this type of

structure.

The solid product from both the top and bottom layers gave primarily B-ethyl-B-diethoxyborazene upon pyrolysis at reduced pressure at temperatures from 100 to 250° C. The formation of this product indicates that there has been cleavage of ethyl ether under the experimental conditions. It is known that Grignard reagents will cleave ethers to form magnesium halide alkoxide, and to place an alkyl radical on the organic group (12). This means that Grignard reagents on the borazene, in cleaving an ether, should form B-alkyl groups according to the equation:

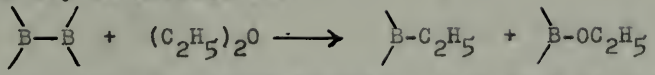
$$\rangle B\text{-}Mg\text{-}Br + (C_2H_5)_2O \longrightarrow \rangle B\text{-}C_2H_5 + MgBr(OC_2H_5)$$

Ether cleavage has been reported by boron trihalides to form alkyl halides and boron trialkoxide (5). If we assume that the boron to bromine bond in a borazene can cleave ethyl ether, B-ethoxy groups will be formed as shown by the equation:

$$\rangle B\text{-}Br + (C_2H_5)_2O \longrightarrow \rangle B\text{-}OC_2H_5 + C_2H_5Br$$

If the course of the reaction between magnesium and B-tribromoborazene is the formation of boron to boron linked polymers of borazene, as postulated above, the boron to boron bond must cleave ethyl ether with a simultaneous cleavage of the boron to boron bond in order to form the pyrolysis product. The equation for the postulated reac-

tion may be written as:



As seen from the above equation, this type of cleavage should produce equal numbers of B-ethyl and B-ethoxy groups.

From the foregoing considerations, a polymer of borazene rings with the third boron site occupied by a magnesium bromide group should produce B-diethyl-B-ethoxyborazene when cleaving ethyl ether, whereas the predominant product was B-ethyl-B-diethoxyborazene. However, the discussion above was based on the average composition of the mixture and not upon the composition of specific units in the mixture. In addition, the pyrolysis product is formed in relatively small yields (10 to 15 per cent), indicating that only a fraction of the bonds in the mixture are ruptured.

Solvents other than ethyl ether may be used for the preparation of the Grignard reagent (12). It has been found that some Grignard reagents which form only with great difficulty in ethyl ether form readily in tetrahydrofuran. An attempt to use tetrahydrofuran as a solvent for the reaction of B-tribromoborazene with magnesium failed because of the vigorous reaction between tetrahydrofuran and B-tribromoborazene. This reaction will be discussed more fully later in this section.

The use of tetrahydrofuran as a solvent for N-trimethyl-B-trichloroborazene, in the presence of magnesium and iodine, led to a slow reaction between magnesium and N-trimethyl-B-trichloroborazene. Analysis of the reaction product was consistent with a borazene containing boron to magnesium to chlorine bonds. This reaction needs to be studied more fully.

In an attempt to prepare the Grignard reagent of N-trimethyl-B-trichloroborazene by an exchange reaction with previously prepared ethyl magnesium bromide, it was discovered that N-trimethyl-B-trichloroborazene undergoes a rapid, exothermic coupling with Grignard reagents to form B-alkyl substituted borazenes. This has been established as a practical synthesis for the preparation of B-alkyl and B-allylborazenes in good yield. The reaction appears to be stepwise according to the equations:

$$N_3(CH_3)_3B_3Cl_3 + RMgX \longrightarrow N_3(CH_3)_3B_3Cl_2R + MgClX$$

$$N_3(CH_3)_3B_3Cl_2R + RMgX \longrightarrow N_3(CH_3)_3B_3ClR_2 + MgClX$$

$$N_3(CH_3)_3B_3ClR_2 + RMgX \longrightarrow N_3(CH_3)_3B_3R_3 + MgClX$$

For the case where R is C_4H_9 the intermediates could be isolated. For the case where R is C_2H_5 , or $-CH_2-CH=CH_2$, only mixtures of the intermediates could be isolated. The fact that both mono- and di-(n-butyl) derivatives can be obtained in reasonable yields from the same reaction mix-

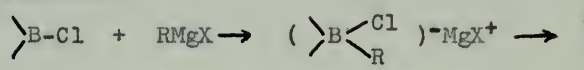
ture seems to indicate that alkyl substitution on one boron atom does not profoundly affect the rate for the next reaction step. A comparison of calculated product ratios expected from a series of consecutive reactions with the same reagent, with the yields obtained for the n-butyl derivatives, further suggests that the relative specific rates of the individual steps are mainly determined by the statistical distribution of the halogen on the borazene rings, and possible changes in activation energies would be slight. However, more extensive work is necessary before this can be established definitely.

Addition of the N-trimethyl-B-trichloroborazene to the Grignard reagent gave a poor yield of product. In general, it was necessary to add the Grignard reagent to an excess of the borazene to give satisfactory results.

The reaction of the Grignard reagent with B-trichloroborazene gives poorer yields than in the case of N-methyl substitution. Similarly the reaction of Grignard reagent with B-tribromoborazene gives poor yields of B-trialkylborazenes. If less than three moles of Grignard reagent is used for each mole of B-tribromoborazene, no partially substituted B-alkyl-B-bromoborazenes can be recovered. There are several ways in which the yield can be decreased. The Grignard reagent could react with the active hydrogen on

the nitrogen to form Grignard salts on the nitrogen. Also, the Grignard reagent might exchange functional groups with the B-tribromoborazene to form a Grignard reagent on the borazene. This could then polymerize as it presumably did when magnesium was reacted with B-tribromoborazene.

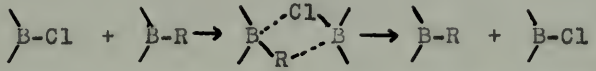
The path of the reaction between Grignard reagents and B-haloborazenes may be postulated as proceeding through a tetracovalent boron complex (13) that has been mentioned in a preceding part of the discussion according to the equation:



There has been evidence in this research for disproportionation of B-unsymmetrical borazenes. In attempts to prepare unsymmetrical N-trimethyl-B-chloro-B-ethylborazene only mixtures of the possible unsymmetrical products were distilled. During attempted fractionation N-trimethyl-B-trichloroborazene was formed. When the pyrolysis product from the reaction of magnesium with B-tribromoborazene was allowed to stand for three months at room temperature, it was found that a liquid with a boiling point range of 56 to 76° C. (.35 mm. Hg) was formed. Originally the liquid had a boiling point of 66° C. (.4 mm. Hg). Apparently the original liquid, B-ethyl-B-diethoxyborazene, had disproportionated to the other possible products.

The inability to isolate pure derivatives containing

both B-ethyl and B-chloro substitution on the borazene ring may be attributed to a redistribution equilibrium that is disturbed during the separation. On the other hand, the n-butyl derivatives were sufficiently resistant to redistribution to permit the separation of the unsymmetrical compounds of the mixture. A bridged dimer transition state (14, 15) may be proposed according to the following equation:



For this type of transition state it is reasonable to suppose that an ethyl group will form an alkyl bridge more readily than a n-butyl group, considering the decrease of stability of aluminum trialkyl dimers with increase in the length of the alkyl group (17). Since B-ethyl-B-diethoxyborazene did not disproportionate upon distillation, it would appear that the B-ethoxy group is less prone to form the bridged transition state than is the B-chloro group.

Borazene and its compounds may possibly form addition products of the Lewis acid-base type. In principle, borazene and its derivatives should be able to function either as Lewis acids, because of empty orbitals present on the boron atoms, or as Lewis bases because of electron pairs on the nitrogen atoms which are not used in bonding. For example, it has been found that borazene and diethyl ether form an addition compound, making separation diffi-

cult (24). Because nitrogen is bonded to boron in the ring, there can be internal dative bonds formed to give a resonance structure similar to the one proposed for benzene by Kekule. The extent of internal double bonding has not been determined, but will, of course, depend upon the substituents present on the ring. Donor atoms present on the boron will reduce the donor-acceptor bonding present in the ring.

In the present research, it has been shown that tetrahydrofuran and B-tribromoborazene react exothermically in benzene, ethyl ether, or without solvent to produce a white or light-colored precipitate from which B-tribromoborazene may not be recovered. Heating this product at reduced pressure results in the formation of a liquid with a wide boiling point range. The stoichiometry of the solid addition compound has been established as one mole of B-tribromoborazene to three moles of tetrahydrofuran, so apparently the tetrahydrofuran has added to the three boron positions on the ring. It is probable that at higher temperatures tetrahydrofuran may be cleaved, resulting in B-alkoxy or B-alkyl substitution on the borazene ring, and it is these substitution products which form the liquid found upon heating. Tetrahydrofuran should have less steric hindrance than ethyl ether for the formation of addition compounds, which could explain why no stable addition compounds

are formed from ethyl ether and B-tribromoborazene.

The reaction of boron tribromide with methylamine hydrochloride gave an unexpectedly low yield of a N-trimethyl-B-trihaloborazene containing considerable amounts of chlorine. The results can be discussed from several points of view. The product could be unstable and, therefore, could have decomposed during the reaction period. This argument was used to rationalize the low yields of B-trichloroborazene and B-tribromoborazene. However, there is no reason to expect a marked difference in stability between N-trimethyl-B-trichloroborazene and N-trimethyl-B-tribromoborazene. The product formed seemed as stable when stored as was N-trimethyl-B-trichloroborazene. It seems, therefore, as if the low yield is due to a lack of formation of the N-trimethyl-B-tribromoborazene. This can be ascribed to several different factors, which are discussed in the following paragraphs.

Lapine Models of the possible intermediates in the reaction show that a certain amount of strain would be present in the intermediates. This could increase the activation energy for the reaction, thereby decreasing the reaction rate. Steric strain can not rule out the formation of the intermediate containing only bromine, since it is known that N-trimethylborazene will add three moles of bromine (22). The third mole is added very slowly, probab-

ly because of steric strain. This addition product would be more strained than any intermediate in the formation of N-trimethyl-B-tribromoborazene. Therefore steric strain may decrease the rate of reaction, but it should not prevent the reaction from occurring.

The ratio of chlorine to bromine found in the product was approximately one to one, whereas the ratio in the reactants was one to three. This indicates that the rate of formation of the B-chloro product is at least three times the rate of formation of the B-bromo product. Since hydrogen chloride and boron trichloride are more volatile than hydrogen bromide or boron tribromide, the chloro compounds would be preferentially lost by the system. This would have the effect of increasing the ratio of rates above the minimum value of three to one. If the frequency factor in the Arrhenius equation is assumed to be the same for both reactions, we obtain, by taking the ratio of the rate equations:

$$\frac{3}{1} = e^{-\Delta E/RT}$$

Assuming T to be 130° C., we find ΔE is equal to 876 calories per mole. This is a minimum value for the differences of overall activation energies for the two reactions.

The presence of B-chloro groups necessitates an exchange of bromine for chlorine at one or several places in the reaction. Boron tribromide could exchange with the

chlorine atom in methylamine hydrochloride, boron tribromide could exchange with hydrogen chloride released from the reaction of boron tribromide with methylamine hydrochloride, or exchange could occur at other points in the reaction sequence. Because of the volatility of hydrogen chloride, exchange must occur during the first part of the reaction. To calculate the feasibility of extensive exchange in the system, the free energy change for the reaction between hydrogen chloride and boron tribromide will be calculated according to the equation:

$$3HCl + BBr_3 \longrightarrow 3HBr + BCl_3$$

The value for ΔF°_{298} for the above compounds are: BBr_3 = -51 kcal./mole, BCl_3 = -93.5 kcal./mole, HCl = -22.74 kcal./mole, and HBr = -12.54 kcal./mole (6). Using these values, we find that ΔF for the reaction with all components gaseous and in their standard states is -12.9 kcal. for the reaction as written above. From this the equilibrium constant is calculated to be 6.3×10^9. Assuming that there is no major change in the free energy differences to a temperature of 400° C., we see that the equilibrium for the exchange reactions discussed above should be far to the right. Since the bridged dimer transition state mentioned earlier provides a ready kinetic path for the exchange, equilibrium should be achieved readily.

It can be seen from the foregoing discussion that chlorine substitution on the borazene ring is the result of the overall chemistry of the system rather than exclusively steric effects. The fact that the reaction times for the formation of B-trichloroborazene and B-tribromoborazene are the same, despite the presence of boron tribromide in much larger concentration, supports the conclusion that steric effects alone can not be used to explain the low yield of N-trimethyl-B-tribromoborazene. It seems probable that a major extension of the reaction time, or temperature, should raise the yield in the reaction.

CONCLUSION

It has been demonstrated that Grignard reagents react with B-haloborazenes to form B-alkylborazenes. Better yields are obtained if there is N-trimethyl substitution of the borazene. This work has been confirmed by results of other laboratories after the inception of this research (7). It has been shown that this reaction is applicable to the formation of condensation polymers of borazene rings.

It has been established that B-haloborazenes will react with ~~metals~~ magnesium under the proper conditions. More work is necessary to clarify the course of this reaction. The hypothesis set forth for the reaction between magnesium and B-tribromoborazene could be placed on a firmer basis by the preparation of B-monobromoborazene followed by its reaction with magnesium. A dimer which could be easily evaluated should be formed. The reactivity of the product of the reaction should be established. The present work has indicated reactivity toward acetone, dry-ice, and Grignard reagents. These reactions need further study.

This research has shown that B-trihaloborazenes will cleave aliphatic and cyclic ethers. This cleavage has previously been reported for boron trihalides (5). Further study of this reaction should be fruitful.

The reactivity of B-haloborazenes toward other met-

als should be found. A small scale experiment in these laboratories indicates that sodium reacts with N-trimethyl-B-trichloroborazene.

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BIOGRAPHICAL SKETCH

James J. Harris was born in Chicago, Illinois, on January 27, 1930. He received his primary education in Elmhurst, Illinois, and his secondary education in Angola, Indiana.

In September 1948 he entered Miami University, Oxford, Ohio, where he received a Bachelor of Arts degree cum laude in June 1952. In June 1953 he received a Master of Science degree from Miami University. While at Miami University he held a Cottrell Fellowship in Chemistry.

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He is a member of Phi Eta Sigma, Sigma Pi Sigma,

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COMMITTEE REPORT

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 9, 1958

C. T. Byrns
Dean, College of Arts and Sciences

Dean, Graduate School

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